









Stephen Beszant, Elios Giannini, Giuseppe Zanoni and Giovanni Vidari\*

Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88% (GC)  $[\alpha]_{D}^{20} = +30.3 \ (c \ 1.1, \ CH_{2}Cl_{2})$ Source of chirality: enantioselective synthesis Absolute configuration: (S)

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Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 87.5% (HPLC) E:Z = 24.4:1 $[\alpha]_{D}^{20} = +230 \ (c \ 1.40, \ CH_{2}Cl_{2})$ Source of chirality: enantioselective synthesis Absolute configuration: (S)

Stephen Beszant, Elios Giannini, Giuseppe Zanoni and Giovanni Vidari\* E.e. 96.7% (GC)



C13H20O

(S)-y-Damascone

C13H20O

(S)- $\gamma$ -Ionone

C10H14O2 (1R,5S)-Karahana lactone

Tetrahedron: Asymmetry 13 (2002) 1245

 $[\alpha]_{D}^{20} = +260.5 \ (c \ 0.90, \ CH_{2}Cl_{2})$ Source of chirality: enantioselective synthesis Absolute configuration: (1R, 5S)

Tetrahedron: Asymmetry 13 (2002) 1241



 $C_{14}H_{28}O_4Si$ Methyl (6*R*)-(*Z*)-6,7-dihydroxy-7-methyl-3-(trimethylsilyl)methyl-2-octenoate

Stephen Beszant, Elios Giannini, Giuseppe Zanoni

and Giovanni Vidari\*

ГMS

COOMe

Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88%[ $\alpha$ ]<sub>D</sub><sup>20</sup>=+0.52 (*c* 2.78, CH<sub>2</sub>Cl<sub>2</sub>) Source of chirality: enantioselective synthesis Absolute configuration: (*S*)



Stephen Beszant, Elios Giannini, Giuseppe Zanoni and Giovanni Vidari\* Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88%  $[\alpha]_{D}^{20} = +109 \ (c \ 0.78, \ CH_2Cl_2)$ Source of chirality: enantioselective synthesis Absolute configuration: (2S, 6R)

 $C_{11}H_{18}O_3 \label{eq:c11}$  Methyl (2S,6R)-(+)-cis-2-hydroxy- $\gamma$ -cyclogeraniate

COOMe

HO

Stephen Beszant, Elios Giannini, Giuseppe Zanoni and Giovanni Vidari\*

Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88%  $[\alpha]_{D}^{20} = +46.6$  (c 1.02, CH<sub>2</sub>Cl<sub>2</sub>) Source of chirality: enantioselective synthesis Absolute configuration: (2*S*,6*R*)

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Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88%[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +24.9 (*c* 0.73, CH<sub>2</sub>Cl<sub>2</sub>) Source of chirality: enantioselective synthesis Absolute configuration: (*S*)

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Tetrahedron: Asymmetry 13 (2002) 1245

E.e. 88%[ $\alpha$ ]<sub>D</sub><sup>20</sup>=+290 (*c* 1.11, CH<sub>2</sub>Cl<sub>2</sub>) Source of chirality: enantioselective synthesis Absolute configuration: (*S*)

 $C_{13}H_{20}O$ (S)-1-(2',2'-Dimethyl-6'-methylene-1'-cyclohexyl)-but-3-en-1-one (+)-**23** 

L. Minuti,\* A. Taticchi,\* C. Rosini,\* D. Lanari, A. Marrocchi, and S. Superchi  $\begin{array}{c} \hline \\ \hline \\ \hline \\ C_{28}H_{34}N_2O_2 \end{array}$ 

 $(S,S)-(-)-(2Z)-2-(1-\{[2-(Methoxymethyl)-pyrrolidin-1-yl]amino\}ethylidene)-2,3,6,11,12,13-hexahydro-1H,5H-4,14-ethanediylidene-7,10-ethenocyclopenta[13]annulen-1-one$ 

 $C_{10}H_{18}O$ (S)-(+)- $\gamma$ -Cyclogeraniol

H<sub>2</sub>OH

 $C_{10}H_{18}O_2$ 

(2S,6R)-(+)-cis-2-Hydroxy-γ-cyclogeraniol

HC













 $\label{eq:C22} C_{22}H_{21}N_3O_5$ l-(4-Methylphenyl)-3-methoxycarbonyl-5-(S)-[1-(2-oxo-5-(S)-phenyl-4,5-dihydro)oxazolo]carbonyl-4,5-dihydropyrazole



 $[\alpha]_{D}^{25} = -8.6$  (c 1.85, CHCl<sub>3</sub>) Source of chirality: (1*S*,2*R*)-(-)-2,10-camphorsultam Absolute configuration: 5*S* 

 $C_{23}H_{29}N_3O_5S$ 

MeOO

1-(4-Methylphenyl)-3-methoxy carbonyl-5-(S)-[N-(1S,2R)-2,10-camphorsultamo] carbonyl-4,5-dihydropyrazole

Luisa Garanti, Giorgio Molteni\* and Tullio PilatiTetrahedron: Asymmetry 13 (2002) 1285MeOOC $[\alpha]_D^{25} = +80.4 (c \ 0.20, CHCl_3)$ <br/>Source of chirality: L-proline methyl ester<br/>Absolute configuration: 5RMeOOC $C_{19}H_{23}N_3O_5$ 1-(4-Methylphenyl)-3-methoxycarbonyl-5-(R)-[1-(2-(S)-methoxycarbonyl)pyrrolidino]carbonyl-4,5-dihydropyrazole

Luisa Garanti, Giorgio Molteni\* and Tullio PilatiTetrahedron: Asymmetry 13 (2002) 1285MeOOC $[\alpha]_D^{25} = +76.3 (c \ 0.19, CHCl_3)$ <br/>Source of chirality: L-proline benzyl ester<br/>Absolute configuration: 5R $K_{25}H_{27}N_3O_5$  $S_{25}H_{27}N_3O_5$ 

1-(4-Methylphenyl)-3-methoxycarbonyl-5-(R)-[1-(2-(S)-benzyloxycarbonyl)pyrrolidino]carbonyl-4,5-dihydropyrazole

Luisa Garanti, Giorgio Molteni\* and Tullio Pilati

Tetrahedron: Asymmetry 13 (2002) 1285

 $[\alpha]_{D}^{25} = -183.2$  (c 0.13, CHCl<sub>3</sub>) Source of chirality: 4-(S)-(+)-phenyl-2-oxazolidinone Absolute configuration: 5*R* 









C22H21N3O5

Luisa Garanti, Giorgio Molteni\* and Tullio Pilati

HOOC

Tetrahedron: Asymmetry 13 (2002) 1285

 $[\alpha]_{D}^{25} = +109.0 \ (c \ 0.10, \ \text{CHCl}_{3})$ Source of chirality: chiral precursor Absolute configuration: 5R

C17H19N3O5 1-(4-Methylphenyl)-3-carboxy-5-(R)-[1-(2-(S)-carboxy)pyrrolidino]carbonyl]-4,5-dihydropyrazole

Luisa Garanti, Giorgio Molteni\* and Tullio Pilati Tetrahedron: Asymmetry 13 (2002) 1285  $[\alpha]_{D}^{25} = +5.5 \ (c \ 0.40, \ DMSO)$ Source of chirality: chiral precursor HOOC Absolute configuration: 5S соон Τo  $C_{12}H_{12}N_2O_4$ 1-(4-Methylphenyl)-3-carboxy-5-(S)-carboxy-4, 5-dihydropyrazole















Absolute configuration: R,R

C<sub>27</sub>H<sub>25</sub>NO<sub>2</sub>

N-[(R)-(2-Hydroxynaphthalen-1-yl)phenylmethyl]-N-((1'R)-1'-phenylethyl)acetamide

Yi Wang, Xin Li and Kuiling Ding\* Tetrahedron: Asymmetry 13 (2002) 1291  $[\alpha]_D^{20} = +81.7 (c \ 0.61, CHCl_3)$ Source of chirality: enantiomerically pure starting material  $C_{28}H_{24}F_3NO_4S$ 1-{(R)-[Acetyl((1'R)-1'-phenylethyl)amino]phenylmethyl}naphthalen-2-yl trifluoromethanesulfonate

















Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100%  $[\alpha]_D^{20} = -200 \ (c \ 1, CHCl_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1*R*,5*S* 

(1R,5S)-3-Acetyl-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one

Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Tetrahedron: Asymmetry 13 (2002) 1299 Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100% $[\alpha]_{\rm D}^{20} = -277$  (c 1.02, CHCl<sub>3</sub>) Source of chirality: (-)-cytisine Absolute configuration: 1R,5S C18H18N2O2 (1R,5S)-3-Benzoyl-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Tetrahedron: Asymmetry 13 (2002) 1299 Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100% $[\alpha]_{\rm D}^{20} = -261 \ (c \ 0.95, \ {\rm CHCl}_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1R,5S C16H22N2O2 (1R,5S)-3-(2,2-Dimethylpropionyl)-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Tetrahedron: Asymmetry 13 (2002) 1299 Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100% $[\alpha]_{\rm D}^{20} = -168 \ (c \ 0.28, \ {\rm CHCl}_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1R,5S  $C_{15}H_{20}N_2O_2$ (1R,5S)-3-(2-Methylpropionyl)-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Tetrahedron: Asymmetry 13 (2002) 1299 Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100%  $[\alpha]_{D}^{20} = -284$  (c 1, CHCl<sub>3</sub>) Source of chirality: (-)-cytisine Absolute configuration: 1R,5S,6S C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> (1R,5S,6S)-3-Benzyl-6-propionyl-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one



E.e. = 100%  $[\alpha]_{D}^{20} = -96 \ (c \ 1, \ CHCl_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1R,5S,6S

 $C_{14}H_{18}N_2O_2$ 

 $(1R, 5S, 6S) \hbox{-} 6- Propionyl-1, 2, 3, 4, 5, 6-hexahydro-1, 5-methanopyrido [1, 2-a] [1, 5] diazocin-8-one and a straight of the straight o$ 



Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Jean-Christophe Plaquevent and Marie-Claire Lasne E.e.=100% $[\alpha]_D^{20}=-151 (c 1.12, CHCl_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1*R*,5*S*,6*S* (1*R*,5*S*,6*S*)-8-Oxo-1,3,4,5,6,8-hexahydro-2*H*-1,5-methanopyrido[1,2-*a*][1,5]diazocin-6-carboxylic acid methyl ester



 $C_{21}H_{24}N_2O_2 \label{eq:C21} (1R,5S,6R)-3-Benzyl-6-propionyl-1,2,3,4,5,6-hexahydro-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (1,2-a)[1,5]diazocin-8-one (1,5-a)[1,5]diazocin-8-one (1,5-a)[1,5]diazocin-8-one (1,5-a)[1,5]diazocin-8-one (1,5-a)[1,5]diazocin-8-one (1,5-a)[1,5-a][1,5]diazocin-8-one (1,5-a)[1,5-a][1,5]diazocin-8-one (1,5-a)[1,5-a][1,5]diazocin-8-one (1,5-a)[1,5-a][1,5]diazocin-8-one (1,5-a)[1,5-a][1,5]diazocin-8-one (1,5-a)[1,5-a][1,5$ 

Jacques Rouden,\* Alexis Ragot, Sonia Gouault, Dominique Cahard, Jean-Christophe Plaquevent and Marie-Claire Lasne E.e. = 100% $[\alpha]_{D}^{20} = -141 (c \ 0.45, \ CHCl_3)$ Source of chirality: (-)-cytisine Absolute configuration: 1*R*,5*S*,6*R* (1*R*,5*S*,6*R*)-3-Benzyl-8-oxo-1,3,4,5,6,8-hexahydro-2*H*-1,5-methanopyrido[1,2-*a*][1,5]diazocin-6-carboxylic acid methyl ester

















 Javier González-Sabín, Vicente Gotor\* and Francisca Rebolledo\*
 Tetrahedron: Asymmetry 13 (2002) 1315

 E.e. 96% (HPLC, Chiralcel-OD)
  $[\alpha]_{20}^{20} = +33.5 (c \ 1.00, CHCl_3)$  

 Source of chirality: enzymatic resolution

 Absolute configuration: S

 González-Sabín, Vicente Gotor\* and Francisca Rebolledo\*

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Enantiopure (HPLC, Chiralcel-OD)  $[\alpha]_D^{20} = +29.8 \ (c \ 1.05, \ CHCl_3)$ Source of chirality: enzymatic resolution Absolute configuration: *R* 

 $C_{12}H_{17}NO_2$ (*R*)-*N*-[1-(*o*-Methoxyphenyl)propan-2-yl]ethanamide

NHAc

Javier González-Sabín, Vicente Gotor\* and Francisca Rebolledo\* E.e. 98% (HPLC, Chiralcel-OD)  $[\alpha]_D^{20} = +37.6 (c \ 1.00, CHCl_3)$ Source of chirality: enzymatic resolution Absolute configuration: R R

José L. García Ruano,\* M. Ángeles Fernández-Ibáñez, Ana M. Martín Castro,\* Jesús H. Rodríguez Ramos and Ana C. Rubio Flamarique

C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (2*R*,3*R*)-3-Cyano-2-hydroxy-2-isopropylbutanamide

Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%

 $[\alpha]_{D} = -9.57$  (c 0.31, acetone) Source of chirality: stereoselective synthesis Absolute configuration: 2R, 3R

Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%  $[\alpha]_{\rm D} = +20.6 \ (c \ 0.4, \ acetone)$ Source of chirality: stereoselective synthesis Absolute configuration: 2R,1'S

OH H2NOC  $C_8H_{14}N_2O_2$ (2R)-2-[(1S)-Cyanoethyl]-2-hydroxy-2-pentanamide

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Tetrahedron: Asymmetry 13 (2002) 1321

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 $C_8H_{14}N_2O_2$ (2R)-2-[(1R)-Cyanoethyl]-2-hydroxy-2-pentanamide

E.e. >97%  $[\alpha]_{\rm D} = -14.2$  (c 0.5, acetone) Source of chirality: stereoselective synthesis Absolute configuration: 2R,1'R

Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%  $[\alpha]_{\rm D} = +54.2$  (c 0.2, acetone) Source of chirality: stereoselective synthesis Absolute configuration: 2R,3S

 $C_6 H_{10} N_2 O_2$ (2R,3S)-3-Cyano-2-hydroxy-2-methylbutanamide

Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%

 $[\alpha]_{\rm D} = -11.8$  (c 0.15, CHCl<sub>3</sub>) Source of chirality: stereoselective synthesis Absolute configuration: 2R

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> (2R)-3-Cyano-2-hydroxy-2-methylpropanamide

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Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%  $[\alpha]_D = -13.4$  (*c* 0.09, CHCl<sub>3</sub>) Source of chirality: stereoselective synthesis Absolute configuration: 2*S* 

H<sub>2</sub>NOC C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (2S)-3-Cyano-2-hydroxy-2-methylpropanamide

OН

 $C_{10}H_{10}N_2O_2$ 

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(2S)-3-Cyano-2-hydroxy-2-phenylpropanamide

José L. García Ruano,\* M. Ángeles Fernández-Ibáñez, Ana M. Martín Castro,\* Jesús H. Rodríguez Ramos and Ana C. Rubio Flamarique Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%  $[\alpha]_D = -23.2$  (*c* 0.12, CHCl<sub>3</sub>) Source of chirality: stereoselective synthesis Absolute configuration: 2*S* 

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Ana M. Martín Castro,\* Jesús H. Rodríguez Ramos and

Ion Neda,\* Thomas Kaukorat and Christian-George Hrib

Tetrahedron: Asymmetry 13 (2002) 1321

E.e. >97%  $[\alpha]_{D} = -14.7$  (c 0.2, CHCl<sub>3</sub>) Source of chirality: stereoselective synthesis Absolute configuration: 2S

 $C_8H_{14}N_2O_2$ (2S)-2-Cyanomethyl-3,3-dimethyl-2-hydroxybutanamide

Tetrahedron: Asymmetry 13 (2002) 1327

 $[\alpha]_{D}^{20} = -28.1$  (*c* 1, EtOH) Source of chirality: homochiral starting material Absolute configuration: 1S, 2S, 4S, 5R

 $\label{eq:c10} C_{10}H_{20}N_2 \\ (1S,2S,4S,5R)-2-(Aminomethyl)-5-ethyl-1-azabicyclo[2.2.2]octane$ 







Aldo Taticchi,\* Lucio Minuti,\* Assunta Marrocchi, Daniela Lanari, and Eszter Gacs-Baitz  $\begin{array}{c} Tetrahedron: Asymmetry 13 (2002) 1331\\\\ \hline\\ E.e. >99\%\\ [\alpha]_D = -820 (c \ 0.096, CHCl_3)\\\\ Source \ of \ chirality: (S)-(+)-4-ethenyl[2.2]-\\paracyclophane\\\\\hline\\ (R)-(-)-2,3,8,9,11,12-Hexahydro-1,10:4,7-diethenocyclododeca[a]anthracene-13,18-dione\\\end{array}$ 



(R)-(+)-17-Hydroxy-2,3,8,9-tetrahydro-1,10:4,7-diethenocyclododeca[a]anthracene-13,18-dione



